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(54) **Coated substrate for tranparent assembly with high selectivity**

(57) A coated sheet for use in a laminated assembly, and a process for making such a sheet, is provided by a transparent substrate carrying two metal layers formed of silver or silver alloy with metals such as Pt and Pd and three layers of a transparent dielectric non-absorbent material, in the sequence, from the substrate: non-absorbent 1/metal 1/non-absorbent 2/metal 2/non-absorbent 3, wherein the total geometrical thickness of the metal layers is in the range 16.5 to 22 nm, the optical thickness of the non-absorbent 1 layer is in the range 50 to 56 nm, the total optical thickness of the non-absorbent layers is in the range 220 to 260 nm and the thickness ratio non-absorbent 2:non-absorbent 1 is in the range 2.1:1 to 2.8:1. The assembly incorporating the coated sheet provides luminous transmission of up to at least 75%, energy transmission of less than 42% and has a pleasant colour aspect.

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Coated substrate for transparent assembly with high selectivity

This invention relates to a coated substrate, in particular to a coated transparent sheet providing a laminated assembly with a high selectivity, i.e. a high ratio of luminous transmission to energy transmission.

Laminated assemblies comprising coated substrate sheets which provide the assemblies with high selectivity have become much used for vehicle windows, especially for motor cars and railway carriages. These duties pose the conflicting needs of providing adequate light transmission, in many instances as defined by legal regulations, while protecting the vehicle occupants against solar radiation. Desirably the window also presents a pleasing tint to the vehicle occupants and passers-by.

Several of the terms used for the properties of a coated substrate have precise meanings defined by an appropriate standard. Those used herein include the following, most of them as defined by the International Commission on Illumination - *Commission Internationale de l'Eclairage* ("CIE").

In the present specification, two standard illuminants are used: Illuminant C and Illuminant A, as defined by CIE. Illuminant C represents average daylight having a colour temperature of 6700 K. Illuminant A represents the radiation of a Planck radiator at a temperature of about 2856 K. This illuminant represents the light emitted by car headlamps and is essentially used to evaluate the optical properties of glazing panels for motor vehicles.

The term "luminous transmission" (TLA) used herein is as defined by CIE, namely the luminous flux transmitted through a substrate as a percentage of the incident luminous flux of Illuminant A.

The term "energy transmission" (TE) used herein is as defined by CIE, namely the total energy directly transmitted through a substrate without change in wavelength. It excludes the absorbed energy (AE), i.e. the energy which is absorbed by the substrate.

The term "selectivity" (SE) used herein is the ratio of luminous transmission (TLA) to energy transmission (TE).

The term "colour purity" used herein refers to the excitation purity measured with illuminant C as defined in the CIE International Lighting Vocabulary, 1987, pages 87 and 89. The purity is specified according to a linear scale on which a defined white light source has a purity of zero and the pure colour has a purity of 100%. For vehicle windows the purity of the coated substrate is measured from the side which is to form the external surface of the window.

The dominant wavelength (λ_D) is the peak wavelength in the range transmitted or reflected by the coated substrate.

The terms "refractive index" and "spectral absorption index" are defined in the CIE International Lighting Vocabulary, 1987, pages 127, 138 and 139.

The substrate is most typically a vitreous material such as glass but can be another transparent rigid material such as polycarbonate or polymethyl methacrylate.

For various reasons, many of them related to considerations of sound or heat transmission or to safety in the event of breakage, the assembly normally comprises two or more laminated sheets. A typical laminated assembly comprises, in sequence, a first layer of glass, a layer of transparent adhesive such as polyvinylbutyral (PVB) and a second layer of glass. The thickness of each glass layer is typically in the range of 1.6 to 3 mm. The mean refractive index of the assembly, ignoring the effect of the coating layers, is typically 1.5. The coating is generally applied to the inner face (i.e. the face in contact with the adhesive) of the sheet that in use will form the external sheet of the assembly, but it can alternatively be applied to the inner face of the sheet that in use will form the internal sheet of the assembly.

A laminated assembly tends to have different optical properties from those of a single glass sheet. The differences arise mainly from the use of multiple sheets. Thus the properties required of, and achieved by, a laminated assembly differ from those of a single glass sheet. Care must therefore be taken in manufacturing a laminated assembly to make appropriate selection of the respective materials, thicknesses and coatings so as to ensure that the sought-after properties are achieved.

For road vehicle windows the legal requirement for luminous transmission (TLA) of windshields is at least 70% in USA and at least 75% in Europe. With regard to solar radiation, the total energy

directly transmitted (TE) is desirably well below 50%. A further factor is the colour tint of the coated substrate, which should present a pleasing appearance. A pink tint may be found attractive and a green tint is even more so, which poses an additional problem in achieving the desired colour from the coating while retaining the required high luminous transmission and low energy transmission.

The requirements for railway carriage windows are similar to the above while not in every case so closely regulated by law. The need generally remains to keep the luminous transmission high and the energy transmission low.

For vehicle applications the purity of the reflected colour is preferably low. This has been found to be particularly difficult to achieve simultaneously with a high level of luminous transmission and a low level of energy transmission.

It has become increasingly popular to apply to glass sheets several coating layers, known as a stack, in order to modify their transmission and reflecting properties. Prior proposals have been made for metal and metal oxide layers in many different combinations to serve as the coating stack to impart selected properties to the glass. One recent combination of layers attracting attention has been the so-called "five layer" stack, typically comprising three layers of metal oxide applied alternately with two layers of metal.

US patent 4965121 relates to such a stack for vehicle windshield glass and comprising in sequence from the substrate: a first layer, of dielectric material; a second layer, of partially reflective metallic material; a third layer of dielectric material; a fourth layer, of partially reflective metallic material; and a fifth layer, of dielectric material. The dielectric material is required to have a refractive index of 1.7 to 2.7. The first and fifth layers have substantially the same optical thickness but are 33-45 % of the optical thickness of the third layer. The second and fourth layers have thicknesses within the range of 75-100 % of each other. The claimed stack typically gives a high light transmission and a substantially neutral reflective visible light colour.

French Patent specification 2708926-A1 similarly relates to a five-layer stack, in this case to impart to vehicle or building glass a combination of high selectivity, i.e. a ratio of luminous transmission to energy transmission as high as possible, while retaining a pleasant visual aspect in reflection. It seeks to achieve this purpose by

a stack comprising in sequence from the substrate: a first layer of dielectric material; a first metallic layer with infra-red reflecting properties; a second layer of dielectric material; a second metallic layer with infra-red reflecting properties; and a third layer of dielectric material. The first infra-red reflecting layer has a thickness of 55-57 % of the second infra-red reflecting layer.

We have discovered that the required combination of optical properties sought by the invention may be realised, and other advantages may be obtained, by a five-layer multi-coated substrate in which the coating layers are formed from specific materials within specific thickness limits and with specific ratios in the respective thicknesses of certain layers.

According to the invention there is provided a coated sheet, for use in a laminated assembly having a high level of luminous transmission and a low energy transmission, comprising a transparent substrate carrying two metal layers formed of silver or silver alloy and three layers of a transparent dielectric non-absorbent material, in the sequence, from the substrate: non-absorbent 1/ metal 1/non-absorbent 2/metal 2/non-absorbent 3, wherein the total geometrical thickness of the metal layers is in the range 16.5 to 22 nm, the optical thickness of the non-absorbent 1 layer is in the range 50 to 56 nm, the total optical thickness of the non-absorbent layers is in the range 220 to 260 nm and the thickness ratio non-absorbent 2:non-absorbent 1 is in the range 2.1:1 to 2.8:1.

The invention further provides a process for the production of a coated sheet, for use in a laminated assembly having a high level of luminous transmission and a low energy transmission, which comprises depositing on a transparent substrate two metal layers formed of silver or silver alloy and three layers of a transparent dielectric non-absorbent material, in the sequence, from the substrate: non-absorbent 1/metal 1/non-absorbent 2/metal 2/non-absorbent 3, wherein the total geometrical thickness of the metal layers is in the range 16.5 to 22 nm, the optical thickness of the non-absorbent 1 layer is in the range 50 to 56 nm, the total optical thickness of the non-absorbent layers is in the range 220 to 260 nm and the thickness ratio non-absorbent 2:non-absorbent 1 is in the range 2.1:1 to 2.8:1.

Clear substrates coated according to the invention provide laminated assemblies having the advantageous combination of

luminous transmission of at least 75% and energy transmission of less than 42%. Indeed with certain types of clear glass substrate the energy transmission can be reduced to less than 40%, while retaining the better-than-75% luminous transmission. Such transmission properties make the assemblies highly advantageous as vehicle windshields.

A further desired quality for all glass assemblies used in vehicle windows is a low energy absorption, which should be much less than the energy transmission and energy reflection of the assembly.

The laminated assembly according to the invention also provides for a pleasantly tinted aspect in reflection ranging from pinkish at the lower end (2.10 to 2.40:1) of the defined thickness ratio of non-absorbent 2:non-absorbent 1, to bluish at the upper end (2.70 to 2.80:1). Near the centre of the range (2.45 to 2.65:1) the tinted aspect is greenish, provided that the thickness ratio non-absorbent 3:non-absorbent 1 is in the range 0.85 to 1.10:1. The proviso arises because the coloration is also affected by the thickness ratio non-absorbent 3:non-absorbent 1.

For a vehicle window of the type that includes a black peripheral border applied by serigraphy there is a tendency for a narrow pink band to appear in reflection adjacent to the border. This band, which arises from luminous interference between the coating and the serigraphic border, can be avoided by increasing the oxide layer thicknesses by about 10%.

For a given value of the ratio non-absorbent 2:non-absorbent 1 within the central greenish zone (2.45 to 2.65:1) and a given value of the ratio non-absorbent 3: non-absorbent 1 within the defined range (0.85 to 1.10:1), the dominant wavelength of the laminated assembly increases, i.e. the colour moves towards yellow, when the thickness of the metal 1 layer increases relative to that of the metal 2 layer.

The invention thus provides the further advantage of readily providing the green tint currently favoured for vehicle windows, at the same time as satisfying the demand for high luminous transmission and low energy transmission.

Although the use of clear substrate material is necessary to achieve the required European levels of 75% luminous transmission for vehicle windshield assemblies, the invention includes within its scope the use of at least one substrate sheet which is itself

coloured. For example, for the slightly lower luminous transmission of 70% specified for windshields in USA, assemblies according to the invention including at least one coloured glass sheet can reduce the energy transmission to less than 37%. These assemblies are also well suited to use as road vehicle front side windows. For applications in road vehicle rear side and back windows, assemblies according to the invention including at least one coloured glass sheet provide the combination of luminous transmission of at least 30% and energy transmission of less than 25%.

Assemblies according to the invention further provide levels low luminous reflection, with a maximum reflection of 10% of the incident light. Such low levels of reflection are of especial benefit both for vehicle and architectural applications. High levels of reflected light are uncomfortable for an observer and in the case of road vehicle windows can present a hazard to drivers of other vehicles.

In some instances the coating is most conveniently applied during the glass-forming stage, for example to flat glass sheet in or after a float glass chamber. For vehicle window panels, which generally need to be bent to the shape dictated by the shape of the vehicle bodywork, the coating can either be applied before or after the substrate has been formed and bent into the required shape and size. For vehicle window panels which are coated while still flat and then bent into shape, care must be taken to ensure that the bending action does not harm the coating. The said care may include slightly changing the coating composition or structure to render the coating more capable of withstanding the bending action.

The low thickness of the respective layers of the invention provides operational advantages both in terms of the short time taken to apply the layers and in the economical use of the respective materials.

The total geometrical thickness of the metal layers is preferably in the range 16.5 to 20 nm.

The coating is preferably applied to a face of the substrate sheet that will form an internal surface of the laminated assembly.

The metal layers comprise silver or a silver alloy, such as alloys of silver with platinum or palladium.

The term "non-absorbent material" used herein refers

to a material which has a refractive index [n(λ)] greater than the value of the spectral absorption index [k(λ)] over the whole of the visible spectrum (380 to 780 nm). It is advantageous for the non-absorbent material of the invention to have a refractive index greater than 10 times the spectral absorption index.

Preferably the non-absorbent material has a refractive index measured at 550 nm of between 1.85 and 2.2, advantageously between 1.9 and 2.1.

Suitable non-absorbent materials include oxides such as tin oxide (SnO_2) and zinc oxide (ZnO), nitrides such as silicon nitride (Si_3N_4) or a mixture thereof or a complex of non-absorbent materials such as zinc stannate (Zn_2SnO_4). Zinc oxide is a particularly preferred material due to its high deposit rate, its refractive index - which is well suited to the requirements of the invention - and its beneficial effect on the passivation of the silver layer.

Each complete non-absorbent layer can include more than one of these materials and each layer can be a composite layer formed of successive subsidiary layers of different composition from each other, for example a zinc oxide layer split into two or more sub-layers by one or more layers of another non-absorbent material, such as tin oxide. The sub-layers may be deposited simultaneously and/or successively. It is not essential for the metal and the oxygen or nitrogen in the layer to be present in stoichiometric proportions.

A combination of tin oxide and zinc oxide is generally advantageous, whether in admixture or in successive sub-layers. This seems to be a result of their having very similar refractive indices.

The coated substrate according to the invention may further comprise, as part of a non-absorbent layer, a thin layer of sacrificial material provided above (i.e. subsequently deposited) and in contact with each metal layer. The purpose of the sacrificial material is to protect the silver or silver alloy during deposition of the next non-absorbent layer. Suitable sacrificial materials include titanium and zinc. Titanium is generally preferred because of its being readily oxidisable.

The total optical thickness of the sacrificial material, i.e. the total of the sacrificial material layers in the respective non-absorbent layers, should be not more than 15 nm. When the coating process has been completed substantially the whole of the sacrificial material is present in oxide form.

The coating layers are preferably applied by cathode sputtering. This may be effected by introducing the substrate into a processing chamber containing an appropriate magnetron sputtering source, and provided with entry and outlet gas-locks, a conveyor for the substrate, power sources, sputtering gas inlets and an evacuation outlet. The substrate is transported past the activated sputtering source and cold sputtered by an appropriate atmosphere (oxygen gas in the case of an oxide coating) to give the desired layer on the substrate. The procedure is repeated for each coating layer.

When using this method the use of a sacrificial material is highly desirable in order to protect the metal layer against oxidation during the subsequent deposition of a non-absorbent oxide layer. If however the non-absorbent material is a nitride rather than an oxide, the layer is deposited in an atmosphere of nitrogen and a layer of sacrificial material is not required.

Because silicon nitride is deposited using a cathode of silicon which has been doped, for example with aluminium, nickel, boron, phosphorus and/or tin, the dopant element(s) may be present in the non-absorbent material layer.

The coating layers may be completed by a thin (2-5 nm) protective layer which shields the coating without significantly modifying the optical properties of the product. Otherwise the third non-absorbent layer will usually be an exposed layer. Suitable materials for the thin exposed protective additional layer are oxides, nitrides and oxynitrides of silicon. Silica (SiO_2) is the generally preferred material. This layer provides the coated substrate with improved chemical and/or mechanical durability, with little or no consequential change in its optical properties.

Glazing panels comprising the laminated assemblies of the invention may be installed in single or multi-glazed units, for example as double-glazing units or windshields for vehicles.

One version of multiple glazing unit for a vehicle comprises a laminated assembly according to the invention positioned in face-to-face spaced apart relationship with a sheet of transparent vitreous material and having a gas space, delimited by a peripherally extending spacer, between the said assembly and sheet. In this unit the coated surface is directed towards the gas space.

A laminated glazing unit may comprise at least two

sheets of transparent vitreous material secured to each other with the aid of an intervening film of polymer adhesive material, wherein at least one of the sheets is a coated substrate according to the present invention, with the coated surface directed towards the polymer adhesive. Where the coated substrate is used in such a structure the use of a thin protective layer, as discussed above, is desirable to shield the coating and guard against delamination of the coating.

The invention will now be described in more detail, with reference to the following non-limiting examples.

The properties of the coated substrate quoted in the Examples herein were measured on the basis of a laminated assembly comprising, in sequence, a sheet of ordinary soda-lime glass having a thickness of 2.1 mm, a coating on the said sheet, a layer of polyvinylbutyral (pvb) adhesive having a thickness of 0.76 mm and a second sheet of ordinary soda-lime glass having a thickness of 2.1 mm.

EXAMPLES 1-10

Samples of a substrate sheet of 2.1 mm glass were passed though an on-line deposition apparatus comprising two vacuum deposition chambers (at a pressure of 0.3 Pa), a conveyor for the substrate, power sources and gas entry locks. Each deposition chamber contained magnetron sputtering cathodes, sputtering gas inlets and an evacuation outlet, deposition being achieved by passing the substrate sample several times under the cathodes.

The first chamber included cathodes provided with targets formed of zinc and tin, and was employed for the deposition in an oxygen atmosphere of non-absorbent layers of zinc oxide and tin oxide. The second chamber included a silver cathode and a titanium cathode and was employed for the deposition of these metals in an inert (argon) atmosphere, the titanium being required for the deposition of a sacrificial layer. Each substrate sample was subjected to several return passages in order to obtain the desired succession and thickness of coating layers.

The glass used as the substrates was soda-lime glass having a thickness of 2.1 mm and the further properties shown below:

Type of glass	TLA (%)	TE (%)	λ_D (nm)	Purity (%)
Clear (I)	90.6	87.8	571	0.5
Coloured (II)	84.4	67.6	508	1.3
Coloured (III)	80.2	59.5	509	1.8
Coloured (IV)	57.0	44.6	503	3.4

In each case there was applied to the substrate:

a first non-absorbent layer (Ox-1) of zinc oxide and tin oxide,

a first silver layer metal (Ag-1),

a second non-absorbent layer (Ox-2) of zinc oxide, tin oxide and titanium oxide, the latter having an optical thickness of 7.5 nm and being in contact with the first silver metal layer (Ag-1),

a second silver layer (Ag-2),

a third non-absorbent layer (Ox-3) of zinc oxide, tin oxide and titanium oxide, the latter having an optical thickness of 7.5 nm and being in contact with the second silver metal layer (Ag-2).

The so-coated sheets were formed into laminated panels comprising the aforementioned laminated assembly of the coated sheet, a layer of polyvinylbutyral adhesive and a second sheet of 2.1 mm glass. In Examples 1 to 7 both sheets were of clear glass (type I). In Examples 8 to 10 at least one of the sheets was coloured glass (types II, III or IV).

Further details of each of the non-absorbent (Ox-1, Ox-2 and Ox-3) and silver layers (Ag-1 and Ag-2) of the coated sheet and the resultant properties of the coating stack thereby formed are shown in the accompanying Tables.

Table A shows the constituent materials of the non-absorbent layers of the coating stack and their geometrical thicknesses. The Examples 1 to 4 and 8 to 10 present an Ox-1 layer comprising equal thicknesses of SnO_2 and ZnO. The Examples 5 to 7 present an Ox-1 layer always comprising 10 nm of SnO_2 and the rest of the thickness of the said layer being ZnO. The Ox-2 layer of each example is made of the succession TiO_2/ZnO/SnO_2/ZnO/SnO_2/ZnO, the thickness of the extreme sub-layers of ZnO being the same, as well as those of the two sub-layers of SnO_2, these thicknesses being themselves about half of that of the central sub-layer of ZnO. The Ox-3 layer of each example

comprises 2.5 nm of TiO_2 and 10 to 13 nm of SnO_2, the rest of the thickness of the said layer being ZnO.

Table B shows for Examples 1 to 7 the optical thicknesses of each of the layers, the total optical thickness of the non-absorbent layers (Ox-1 + Ox-2 + Ox-3), the ratio of optical thicknesses of the first and second non-absorbent layers (Ox-2:Ox-1), the ratio of optical thicknesses of the first and third non-absorbent layers (Ox-3:Ox-1), and, for the resultant laminated panel, the luminous transmission of Illuminant A (TLA), the energy transmission (TE), the dominant wavelength λ_D, the purity and, where appropriate, the resultant tint. Table C shows similar data to Table B but for Examples 8 to 10 and additionally shows the types of glass employed.

The panels of Examples 1 to 7 are well suited to use as vehicle windshields. The Example 8 panel is well suited to use a vehicle front side window and those of Examples 9 and 10 are well suited to use as vehicle rear windows or rear side windows.

Table A

Example	Ox-1 SnO_2/ZnO (nm)	Ox-2 TiO_2/ZnO/SnO_2/ZnO/SnO_2/ZnO (nm)	Ox-3 TiO_2/ZnO/SnO_2 (nm)
1.	13.1/13.1	2.5/10/10/23/10/10	2.5/13/13
2.	14.0/14.0	2.5/11/11/22.5/11/11	2.5/11.25/11.25
3.	13.4/13.4	2.5/11/11/22.5/11/11	2.5/10/10
4.	13.0/13.0	2.5/10/10/22/10/10	2.5/11/11
5.	10.0/17.0	2.5/11/11/22/11/11	2.5/22/10
6.	10.0/15.0	2.5/10/11/20.5/11/10	2.5/20/10
7.	10.0/15.6	2.5/11/11/21/11/11	2.5/11/10
8.	14.5/14.5	2.5/11/12/24/12/11	2.5/15/10
9.	14.5/14.5	2.5/11/12/24/12/11	2.5/15/10
10.	14.5/14.5	2.5/11/12/24/12/11	2.5/15/10

Table B

Example	Ox-1 ZnO/SnO_2 (nm)	Ag-1 (nm)	Ox-2 ZnO/SnO_2 (nm)	Ag-2 (nm)	Ox-3 ZnO/SnO_2 (nm)	Ox Total (nm)
1.	52.4	8.9	132.0	8.9	58.7	243.1
2.	56.0	9.0	140.7	9.0	51.3	248.0
3.	53.4	8.8	134.7	8.0	46.3	234.3
4.	51.6	9.6	130.1	8.0	50.3	232.0
5.	54.0	8.8	138.3	8.8	70.3	262.6
6.	50.0	8.8	131.3	8.8	66.3	247.6
7.	51.2	8.8	136.1	8.8	48.5	235.8

Example	Ratio Ox-2: Ox-1	Ratio Ox-3: Ox-1	TLA (%)	TE (%)	λ_D (nm)	Purity (%)	Colour
1.	2.52	1.12	76.1	41.3	-493	2	reddish purple
2.	2.51	0.96	76.2	41.0	487	7	greenish blue
3.	2.52	0.88	75.5	40.7	495	2	bluish green
4.	2.52	0.99	75.0	40.6	581	5	greenish yellow
5.	2.56	1.30	76.1	41.1	-554	4	bluish purple
6.	2.63	1.33	75.5	40.5	-542	4	bluish purple
7.	2.66	0.95	75.1	39.9	486	9	greenish blue

Table C

Example	External glass	Adhesive	Ox-1 (nm)	Ag-1 (nm)	Ox-2 (nm)	Ag-2 (nm)	Ox-3 (nm)	Ox Total (nm)	Ratio Ox-2: Ox-1	Internal glass
8.	(I)	pvb	58.4	9.5	146.4	9.5	55.9	260.7	2.51	(II)
9.	(III)	pvb	58.4	9.5	146.4	9.5	55.9	260.7	2.51	(III)
10.	(IV)	pvb	58.4	9.5	146.4	9.5	55.9	260.7	2.51	(IV)

Example	TLA (%)	TE (%)	Colour
8.	70.9	35.6	green
9.	55.0	23.3	green
10.	30.3	14.1	green

CLAIMS

1. A coated sheet, for use in a laminated assembly having a high level of luminous transmission and a low energy transmission, comprising a transparent substrate carrying two metal layers formed of silver or silver alloy and three layers of a transparent dielectric non-absorbent material, in the sequence, from the substrate: non-absorbent 1/metal 1/non-absorbent 2/metal 2/non-absorbent 3, wherein the total geometrical thickness of the metal layers is in the range 16.5 to 22 nm, the optical thickness of the non-absorbent 1 layer is in the range 50 to 56 nm, the total optical thickness of the non-absorbent layers is in the range 220 to 260 nm and the thickness ratio non-absorbent 2:non-absorbent 1 is in the range 2.1:1 to 2.8:1.

2. A coated sheet according to claim 1, which has a thickness ratio of non-absorbent 2:non-absorbent 1 in the range 2.10 to 2.40:1.

3. A coated sheet according to claim 1, which has a thickness ratio of non-absorbent 2:non-absorbent 1 in the range 2.45 to 2.65:1 and which has a thickness ratio of non-absorbent 3:non-absorbent 1 in the range 0.85 to 1.10:1.

4. A coated sheet according to claim 1, in which the thickness ratio of non-absorbent 2:non-absorbent 1 is in the range 2.70:1 to 2.80:1.

5. A coated sheet according to any preceding claim, in which the total geometrical thickness of the metal layers is in the range 16.5 to 20 nm.

6. A coated sheet according to any preceding claim, in which the substrate sheet is itself coloured.

7. A coated sheet according to any one of claims 1 to 5, in which the substrate sheet is clear.

8. A coated sheet according to any preceding claim, in which the metal layers comprise silver or an alloy of silver with platinum or palladium.

9. A coated sheet according to any preceding claim, in which the non-absorbent layer material has a refractive index greater than 10 times the spectral absorption index.

10. A coated sheet according to any preceding claim, in which the non-absorbent layer material has a refractive index measured at 550 nm of between 1.85 and 2.2.

11. A coated sheet according to any preceding claim, in which the non-absorbent material comprises one or more of tin oxide (SnO_2), zinc oxide (ZnO), silicon nitride (Si_3N_4) and zinc stannate (Zn_2SnO_4).

12. A coated sheet according to any preceding claim, in which each non-absorbent layer includes more than one non-absorbent material.

13. A coated sheet according to claim 12, in which each non-absorbent layer comprises tin oxide and zinc oxide.

14. A coated sheet according to claim 12 or claim 13, in which each non-absorbent layer is a composite layer formed of successive subsidiary layers of different composition from each other.

15. A coated sheet according to any preceding claim, comprising, as part of a non-absorbent layer, a thin layer of sacrificial material provided above and in contact with each metal layer.

16. A coated sheet according to claim 15, in which the sacrificial material is selected from titanium and zinc.

17. A coated sheet according to claim 15 or claim 16, in which the total optical thickness of the sacrificial material is not more than 15 nm.

18. A coated sheet according to any preceding claim, further comprising a thin (2-5 nm) outer protective layer of one or more of oxides, nitrides and oxynitrides of silicon.

19. A laminated assembly comprising a coated sheet according to any preceding claim, in which the coating is applied to a face of the substrate sheet that forms an internal surface of the laminated assembly.

20. A laminated assembly according to claim 19, which provides luminous transmission of at least 75% and energy transmission of less than 42%.

21. A laminated assembly according to claim 20, which provides energy transmission of less than 40%.

22. A laminated assembly according to claim 19, which provides luminous transmission of at least 70% and energy transmission of less than 37%.

23. A laminated assembly according to claim 19, which provides luminous transmission of at least 30% and energy transmission of less than 25%.

24. A vehicle windshield comprising a laminated assembly according to any of claims 20 to 22.

25. A double-glazing panel comprising a laminated assembly as claimed in any of claims 19 to 23.

26. A double-glazing panel comprising a laminated assembly according to claim 25, positioned in face-to-face spaced apart relationship with a sheet of transparent vitreous material and having a gas space, delimited by a peripherally extending spacer, between the said assembly and sheet.

27. A process for the production of a coated sheet, for use in a laminated assembly having a high level of luminous transmission and a low energy transmission, which comprises depositing on a transparent substrate two metal layers formed of silver or silver alloy and three layers of a transparent dielectric non-absorbent material, in the sequence, from the substrate: non-absorbent 1/ metal 1/non-absorbent 2/metal 2/non-absorbent 3, wherein the total geometrical thickness of the metal layers is in the range 16.5 to 22 nm, the optical thickness of the non-absorbent 1 layer is in the range 50 to 56 nm, the total optical thickness of the non-absorbent layers is in the range 220 to 260 nm and the thickness ratio non-absorbent 2:non-absorbent 1 is in the range 2.1:1 to 2.8:1.

28. A process according to claim 27, in which the non-absorbent material comprises one or more of tin oxide (SnO_2), zinc oxide (ZnO), silicon nitride (Si_3N_4) and zinc stannate (Zn_2SnO_4).

29. A process according to claim 27 or claim 28, in which each non-absorbent layer is a composite layer formed of successive subsidiary layers of different composition from each other.

30. A process according to claim 29, in which the subsidiary layers within a non-absorbent layer are deposited simultaneously.

31. A process according to any of claims 27 to 30, in which as part of a non-absorbent layer a thin layer of sacrificial material is applied above and in contact with each metal layer.

32. A process according to any of claims 27 to 31, in which the metal layers comprise silver or an alloy of silver with platinum or palladium.

33. A process according to any of claims 27 to 32, in which a thin (2-5 nm) protective layer of one or more of oxides, nitrides and oxynitrides of silicon is applied to the non-absorbent layer 3.

34. A process according to any of claims 27 to 33, in which the coating layers are applied by cathode sputtering.

35. A process according to any of claims 27 to 34, which provides a laminated assembly with luminous transmission of at least 75% and energy transmission of less than 42%.

36. A process according to claim 35, which provides a laminated assembly with energy transmission of less than 40%.

37. A process according to any of claims 27 to 34, which provides a laminated assembly with luminous transmission of at least 70% and energy transmission of less than 37%.

38. A process according to any of claims 27 to 34, which provides a laminated assembly with luminous transmission of at least 30% and energy transmission of less than 25%.

The Patent Office

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Application No: GB 9705499.3
Claims searched: 1-38

Examiner: Peter Beddoe
Date of search: 28 April 1997

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C7F (FPCL, FPCX, FPDL, FPDX)

Int Cl (Ed.6): C03C 17/36; C23C (14/06, 14/18)

Other:

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB 2279365 A	(GLAVERBEL) see esp exs	1,27 at least
X	EP 0709349 A1	(SAINT-GOBAIN) see esp col 5 lines 16-25	1,27 at least
X	EP 0645352 A1	(SAINT-GOBAIN) see esp table 1	1,27 at least
X	EP 0638528 A1	(SAINT-GOBAIN) see esp exs	1,27 at least
X	EP 0488048 A1	(ASAHI) see esp exs	1,27 at least
X	WO 95/29883 A1	(CARDINAL) see esp p4 line 15 - p5 line 6	1,27 at least
X	US 5229881	(TEMPGLASS) see esp col 2 lines 27-68	1,27 at least
X	US 4996105	(ASAHI) see esp col 4 lines 16-36	1,27 at least
X	US 4965121	(BOC) see esp Tables I-IV	1,27 at least

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
& Member of the same patent family
A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.

The Patent Office

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Application No: GB 9705499.3
Claims searched: 1-38

Examiner: Peter Beddoe
Date of search: 28 April 1997

Category	Identity of document and relevant passage	Relevant to claims
X	US 4859532 (ASAHI) see esp ex 5	1,27 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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